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Supporting information for

Assembly of Non-Close-Packed 3D Colloidal Crystal from 2D Ones in Polymer Matrix via in Situ Layer-by-Layer Photopolymerization

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Experimental Section

Materials. Silicon wafer as substrates (10 mm × 10 mm) were cleaned by immersion in piranha solution (7:3 concentrated H_2SO_4 / 30 % H_2O_2) for 1 h at 70 °C to create a hydrophilic surface, and then rinsed repeatedly with Milli-Q water (18.2 MΩ cm^{-1}) and ethanol. The substrates were dried in a nitrogen stream before used. The silica microspheres were prepared by the Stöber method[1] and their average sizes were measured as 1.047 μm and 451 nm, respectively, by SEM with calibrated length. Poly(dimethylsiloxane) (PDMS) elastomer kits (Sylgard 184), were purchased from Dow Corning (Midland, MI). Photoresist Monomers comprise phthalic diglycol diacrylate ($C_{22}H_{26}O_{10}$, PDDA), trimethylolpropane triacrylate ($C_{15}H_{20}O_6$, TMPTA), epoxy acrylate oligomer (EA), and α-hydroxy isobutyryl benzene ($C_{10}H_{12}O_2$, photoinitiator 1173). The four components of photoresist, acetone, sulfuric acid, hydrogen peroxide and poly (vinyl alcohol) (PVA) were used as received. The

equipment used in this system is home-made, which not only in situ adds mechanical pressure on the samples, but also provides the ultraviolet to polymerize.

Preparation.

(1) Fabrication of 2D ncp colloidal crystal

The fabrication process of a monolayer of ncp silica spheres transferred onto the PVA-coated silicon wafer is the same as Ref. 8. The detailed process is as follows. A single layer of hexagonal close-packed (hcp) spheres was transferred to the surface of PDMS film by using the lift-up soft lithography, which was subsequently swollen with the solution of toluene in acetone (in this solution, only toluene, one of nonpolar solvents, was capable of swelling the PDMS film), to transform the hcp array into the ncp one. The obtained 2D ncp array on the deformed PDMS film was transferred to the surface of substrate that was spin-coated with a thin film (~200 nm) of poly(vinyl alcohol) (PVA) by using the modified microcontact printing (μcp) technique. To avoid the influence of PVA on subsequent process, PVA film was decomposed via heating at 500 ℃ for 3 h. Then, 2D ncp colloidal crystal on the silicon substrate was obtained.

(2) Assembly of 2D ncp colloidal crystal

First, about 0.2 ml of the mixtures containing photoresist monomers was spun onto the surface of as-prepared silicon spheres at 4000 rpm for 30 s and polymerized by UV light of 250 nm for 90 s. The ratio of four components of monomers is 38.87 wt% (PDDA), 31.75 wt% (EA), 20.28 wt% (TMPTA) and 9.1 wt% (1173). In the mixtures, the volume ratio of the monomers and the dilution, acetone, is 1:0, 1:0.5, 1:1.0, 1:1.5, and 1:2.0, respectively. The mixtures were homogenized at magnetic stirring for approximately 20 min. We unclench the photoresist film at the edge with a knife and the photoresist films peeled off from the substrate with tweezers. Then, the bottom-portion of the spheres that contact with the silicon substrate originally was placed on another single layer of silica spheres which was also covered with the monomers beforehand. Due to the capillary force, the two layers contact each other. This time, the samples were exposed to UV light again going with varying mechanical pressure adding on the films. Repeating these steps, photoresist bulk with desired layer number of colloidal spheres was obtained. All the as-prepared films are about 1 cm ×1 cm,

and the thickness is determined by the layer number of 3D colloidal crystal.

Characterization. Surface and cross-sectional morphologies were investigated by Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM 6700F) with primary electron energy of 3 kV and samples were sputtered with a layer of Pt (ca. 2 nm thick) prior to imaging to improve conductivity. The samples are torn to take cross-sectional morphologies. Kinetic viscosity of the mixture containing the photoresist monomers was measured by Ubbelohde viscometer at 25℃. The viscosity of mixture used polymerizing is obtained by calculation. At least 10 measurements were averaged for all of the data reported here.

Results

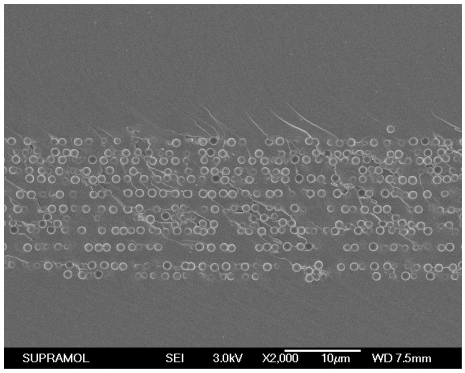

Fig. S1. Cross-sectional SEM image of 3D colloidal crystal with the multi-layer silica spheres.

References

1 W. Stöber, A. Fink and E. Bohn, *J Colloid Interf Sci.,* 1968, **26**, 62.